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OF CRYSTALLINE NH_3 and ND_3

By

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Evidence for One-Dimensional Rotation in Ammonium Iodide

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PREVIOUSLY it has been demonstrated spectroscopically that the λ-point transitions in ammonium halides cannot involve free rotation since the torsional oscillation frequency of the ammonium ion in the lattice occurs in the phase above (*II*) as well as beneath (*III*) the transition temperature.[1] These results were subsequently confirmed by neutron diffraction studies.[2] However, it was noted by Wagner[3] and confirmed by the careful studies by Dinsmore[4] that in the face-centered cubic modification of $NH_4I(I)$, which is stable above the first-order transition at −17.6°C, the combination of the triply degenerate bending vibration ν_4 at 1400 cm^{-1} with the lattice torsion ν_6 which occurs at 1685 cm^{-1} in phases *II* and *III* was absent. Instead the spectra showed only a weak diffuse absorption maximum at 1600–1650 cm^{-1} which persisted without much change in films in which phase *I* was supercooled to −195°C. We have repeated this work with care and found the diffuse region mentioned before at approximately 1600 cm^{-1} and, in addition, noted that there were roughly exponential wings at the base of ν_4 in phase *I*. The width at half-height of the central peak changed from about 23 cm^{-1} in phases *II* and *III* to about 30 cm^{-1} in phase *I*.

These observations are consistent neither with a statically disordered model nor the 3-dimensional freely rotating structure suggested by the heat capacity studies of Stephenson *et al.*[5] The latter would require *P* and *R* branch maxima which do not exist.

According to a rough electrostatic calculation, the minimum potential energy occurs when one N—H bond is directed at an iodine ion. Such a model with free rotation about this N—H···I⁻ axis is consistent with the observed spectrum. The height of the barrier to this rotation, the frequency of the zero-point vibration, and the frequency of the perpendicular torsional oscillation were all computed from the electrostatic potential of an ammonium ion, represented with a charge $+0.43e$ located at the proton positions. This same model has been used successfully to calculate the torsional frequencies in NH_4Cl, NH_4Br, low ND_4Br, and NH_4I (*II* or *III*) and in no case did the effective charge vary outside the limits $0.42e–0.50e$.[6] The calculated torsional frequency was 203

cm^{-1}, in good agreement with the experimental combination band at 1600 cm^{-1}. The height of the barrier to rotation thus calculated was 35 cm^{-1}, with a zero-point vibrational level at 20 cm^{-1}. Consequently, the very first excited level would be above the barrier, and to a good approximation the ion can be thought of as freely rotating when $T > 75°K$.

The selection rules for this model allow only the *Q* branch of the parallel component of ν_4, and only *P* and *R* branches of the perpendicular component, to appear in the infrared spectrum. However, the *P* and *R* branches of a one-dimensional rotator have no maxima; the band envelope is an error function with a missing central line. The predicted envelope of the line fits the experimental curve to within the experimental error and shows the correct effect of temperature on the wings. The diffuse nature of the combination band is roughly accounted for by rotational structure and rotation-vibration interaction.

Consequently, we conclude that the spectrum strongly indicates a structure for phase *I* of NH_4I in which one hydrogen bond is formed to I⁻, and the ammonium ion rotates freely about this bond. A more detailed description of this work will appear at a later date.

Recent neutron diffraction studies of ND_4Br and ND_4I have also led Levy and Peterson to eliminate the model with 3-dimensional free rotation[7]; they find that two different static models and the one-dimensional rotator all give equally good agreement with their data.

* du Pont Fellow in Chemistry, 1951–1952.
[1] E. L. Wagner and D. F. Hornig, J. Chem. Phys. 18, 296 (1950); ibid. 305 (1950).
[2] H. A. Levy and S. W. Peterson, Phys. Rev. 86, 766 (1952).
[3] E. L. Wagner (unpublished data).
[4] H. L. Dinsmore (unpublished data). See also L. F. H. Bovey, J. Opt. Soc. Am. 41, 836 (1951).
[5] Stephenson, Landers, and Cole, J. Chem. Phys. 20, 1044 (1952).
[6] D. F. Hornig and S. Millman (unpublished work).
[7] H. A. Levy and S. W. Peterson, J. Chem. Phys. 21, 366 (1953).

Evidence for One-Dimensional Rotation in NH₄I

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IN a previous communication under this same title[1] it was pointed out that in the NaCl-like phase of NH₄I which exists at room temperature the only reasonable interpretation of the infrared absorption spectrum in the 7μ region led to a model in which the ammonium ion underwent one-dimensional free rotation. It was further concluded that the rotation took place about the hydrogen bond formed from one apex of the NH_4^+ tetrahedron to an adjacent I^- ion.

At the time that note was written we had, unfortunately, overlooked the beautiful investigations of the Raman spectrum of single crystals of NH₄I which had previously been published by L. C. Mathieu and J. P. Mathieu.[2] From measurements of the polarization of the Raman radiation they showed quite definitely that the threefold axis of the NH_4^+ ion coincided with the fourfold axis of the crystal. They did not reach any conclusions regarding rotation of the ion, but their prior evidence is probably less ambiguous than either the infrared spectrum or the neutron diffraction results[3] in demonstrating the one-bond model. Taken together the three investigations make this structure nearly certain.

[1] R. C. Plumb and D. F. Hornig, J. Chem. Phys. 21, 366 (1953).
[2] L. Couture-Mathieu and J. P. Mathieu, J. chim. phys. 49, 226 (1952).
[3] H. A. Levy and S. W. Peterson, J. Chem. Phys. 21, 366 (1953).

THE INFRARED SPECTRUM OF THE OXONIUM ION

Sir:

The infrared absorption spectra of films of oxonium chloride and oxonium bromide have been observed at $-195°$ and spectra which are typical of those obtained are reproduced in Fig. 1. The films were prepared by condensing an equimolar mixture of gaseous H_2O and HX on a previously cooled KBr plate. The OH_3^+ must be the source of the four absorption bands at 1050 cm.$^{-1}$, 1700 cm.$^{-1}$, 2100 cm.$^{-1}$ and 2570 cm.$^{-1}$ in OH_3Cl (similarly, at 1100 cm.$^{-1}$, 1700 cm.$^{-1}$, 2100 cm.$^{-1}$ and 2610 cm.$^{-1}$ in OH_3Br). In addition, some films of both salts show an absorption maximum near 3200 cm.$^{-1}$ as part of the broad absorption region which extends to frequencies above 3500 cm.$^{-1}$. Very little of the observed spectrum can be attributed to ice, whose intense bands[1] at 812 cm.$^{-1}$ and 2150 cm.$^{-1}$,[2] do not appear. Except for the peaks at 2770 cm.$^{-1}$ in OH_3Cl and 2410 cm.$^{-1}$ in OH_3Br, the halides cannot be responsible either since the same bands occur in both salts.
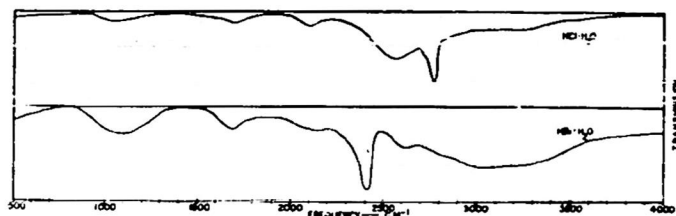

Fig. 1.—The infrared absorption spectrum of oxonium chloride and oxonium bromide at $-195°$.

To confirm these conclusions we have, in addition to the equimolar compounds, condensed five gas mixtures with composition ranging from 90% HCl–10% H_2O to 20% HCl–80% H_2O, and these

showed the expected HCl or ice spectrum superimposed on that of the OH_3^+ ions. The compositions containing excess HCl showed two peaks very close to those reported for pure crystalline HCl at 2704 cm.$^{-1}$ and 2746 cm.$^{-1}$.[3,4] Therefore the HCl responsible for the 2770 cm.$^{-1}$ peak in the OH_3Cl sample must be in a different environment, *e.g.*, as HCl molecules in the OH_3Cl lattice. In this case they may be produced by the equilibrium

$$OH_3Cl \rightleftarrows H_2O + HCl$$
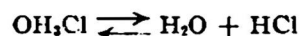
but we have not yet investigated this possibility. Altogether, the general outlines of the experimental situation seem clear, but some details still need clarification. A number of films have been prepared and the spectra were not completely reproducible, differing chiefly in two respects: (a) the shape of the diffuse absorption region between 2350 cm.$^{-1}$ and 3500 cm.$^{-1}$ and (b) the height of the peak we have ascribed to free HX molecules. Further studies are continuing.

Whereas the observed spectrum is different from either ice or the hydrogen halides, it is closely parallel to that of ammonia. The hydrogen stretching frequencies are lower and the bands broader but both of these features may be attributed to strong hydrogen bonds. It may therefore be concluded that the OH_3^+ ion which is isoelectronic with NH_3, also exists in a symmetrical pyramidal configuration. This conclusion agrees with that derived from proton resonance measurements.[5-6]

(1) P. P. Reding, Thesis, Brown University, 1951.

(2) J. J. Fox and A. E. Martin, *Proc. Roy. Soc. (London)*, **A174**, 234 (1940).

(3) G. Hettner, *Z. Physik*, **78**, 141 (1932).

(4) Lee, Sutherland and Wu, *Proc. Roy. Soc. (London)*, **A176**, 493 (1940).

(5) Y. Kakiuchi, *et al.*, *J. Chem. Phys.*, **19**, 1069 (1951).

(6) R. E. Richards and J. A. S. Smith, *Trans. Far. Soc.*, **47**, 1261 (1951).

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VIBRATIONAL SPECTRA OF MOLECULES AND COMPLEX IONS IN CRYSTALS

VII. THE RAMAN SPECTRUM OF CRYSTALLINE AMMONIA AND 3-DEUTERO-AMMONIA

F. P. Reding and D. F. Hornig

ABSTRACT

The Raman spectra of crystalline NH_3 and ND_3 were measured at $-32°C.$, using Hg 2536.5 Å exciting radiation. The fundamentals ν_1, ν_2, and ν_3 were observed but ν_4 was not. ν_2 was split into two components by intermolecular coupling. Lattice frequencies of both translational and rotational origin were observed and there was evidence of very little coupling between them.

THE VIBRATIONAL SPECTRA OF MOLECULES AND COMPLEX IONS IN CRYSTALS

VII. THE RAMAN SPECTRUM OF CRYSTALLINE AMMONIA

AND 3-DEUTERO-AMMONIA

F. P. Reding and D. F. Hornig

INTRODUCTION

The Raman spectrum of crystalline ammonia and 3-deutero-ammonia has been observed in conjunction with the previously reported infrared study of these crystals.[1]

1. F. P. Reding & D. F. Hornig, J. Chem. Phys. 19, 594 (1951)

In that paper it was pointed out that on the basis of the present theory of crystalline spectra[2,3]

2. D. F. Hornig, J. Chem. Phys. 16, 1063 (1948)
3. H. Winston and R. S. Halford, J. Chem. Phys. 17, 607 (1949)

the motions of the four molecules in the unit cell of the cubic ammonia crystal (symmetry T^4) may be expected to couple so that the symmetrical vibrations of NH_3 or ND_3, ν_1 and ν_2, each yield one component of species A and one of species F. Similarly, the doubly degenerate vibrations, ν_3 and ν_4, should each yield one component of species E and two of species F in the crystals. Only the species F components may be active in the infrared spectrum whereas all three (A,E,F) may be active in the Raman spectrum. Actually, although all four fundamentals were observed in the infrared spectrum, only one component arising from each degenerate vibration was observed. In addition, evidence was produced that the second, Raman active, component of ν_1 was displaced by 10 cm^{-1} from the infrared

active component.

Since all ten components arising from the four internal vibrations may be Raman active, it was hoped that the frequency separation between components originating in the different phases of coupling of the four molecules could be determined. This splitting would give a quantitative measure of the intermolecular interaction. In addition, it was hoped that the limiting lattice vibrations, five of which originate in molecular rotation and four in molecular translation, might be observed at low frequencies.

In previous work on the Raman spectrum of crystalline NH_3 Sutherland[4]

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4. G. B. B. M. Sutherland, Proc. Roy. Soc., 141A, 546 (1933)

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reported lines at 3369, 3303, and 1585 cm^{-1} with relative intensities of 4, 1, and 0 respectively. The Raman spectrum of ND_3 was not found in the literature.

<div align="center">EXPERIMENTAL</div>

The ultraviolet absorption spectrum of crystalline NH_3 begins at 2345A.[5]

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5. A. Prikhotko, Acta Physicochimica U.S.S.R. 12, 559 (1940)

Consequently the Hg 2536.5Å proved most satisfactory as an exciting line. The mercury arc used was an eight turn quartz helix. The vapor pressure of the mercury in the lamp was kept low by using amalgamated gold foil electrodes. No evidence of resonance absorption by the cool mercury vapor along the wall of the tube was noted. The exciting line was filtered from the Raman radiation by filling the spectrograph with mercury vapor.

A diagram of the sample tube and cooling jacket is shown in Figure 1. Nitrogen which had been cooled by bubbling through liquid nitrogen was used to cool the Raman tube. In preparation for an investigation, the system was evacuated and the sample condensed from a storage flask into the Raman tube. The liquid was slowly crystallized and a highly cracked semi-transparent crystal was obtained. Since this proved to be satisfactory, no attempt was made to form a flawless single crystal. The NH_3 used[*]

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[*] Mathieson Alkali Works
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was stated to be 99.97 per cent pure. The ND_3 was prepared by the procedure described in the previous paper.

A medium Hilger E-3 303 Spectrograph with quartz optics was used to record the spectra. Depending upon the intensity desired, exposure times varied from 20 minutes to two hours, using a slit of 0.01 mm. The resolution of the spectrometer was approximately three cm^{-1} in the region employed. For wave length determinations, an iron arc spectrum was recorded using a Hartman diaphragm. The error in the measurement of the Raman line displacement was approximately ± 5 cm^{-1}.

RESULTS

The Raman spectra obtained from crystalline NH_3 and ND_3 at -82°C., reproduced from the microphotometer tracings, are shown in Figures 2 and 3, respectively. The mercury lines included are marked and the 2536.5Å exciting line is indicated by A. The frequencies of the band centers and approximate intensities are shown in Table 1. For comparison the fundamental bands observed in the

infrared spectrum are also listed.

Two components of the symmetrical bending vibration ν_2 at 1048 and 1058 cm^{-1} were clearly resolved in the NH$_3$ spectrum. A corresponding doublet was indicated in the ND$_3$ spectrum by the shoulder at 817 cm^{-1} on the high frequency side of the peak at 810 cm^{-1}. From the very near coincidence of the bands at 1058 and 817 cm^{-1} with the corresponding bands for ν_2 in the infrared spectrum, it is safe to conclude that these Raman components arise from the species F vibration. The other two components at 1048 and 810 cm^{-1} in NH$_3$ and ND$_3$ must therefore be the species A components.

The symmetric stretching frequency, ν_1, could not be determined for NH$_3$ because it lies in the broad intense band which extends from 3160 cm^{-1} to 3330 cm^{-1} and has a maximum at approximately 3210 cm^{-1}. This difficulty did not arise for the corresponding line in the ND$_3$ spectrum at 2330 cm^{-1} which is sharp. It is seen in Table 1 that ν_1 in the infrared spectrum of crystalline ND$_3$, which must be of species F, has the band center at 2318 cm^{-1}. The 12 cm^{-1} frequency separation between the infrared and Raman components of this fundamental in ND$_3$ is outside of the experimental error in this region. Consequently these Raman lines probably arise from the species A rather than the species F vibration.

The Teller-Redlich product ratio for the F components of the symmetric vibrations was found to be 1.808 (harmonic value = 1.842). If the product ratio is the same for the A components, ν_1 of NH$_3$ would occur at 3240 cm^{-1}. The broad band in which it is located is apparently the first overtone region corresponding to the intense infrared absorption running from 1575 cm^{-1} to the fundamental ν_4

at 1648 cm^{-1}. A similar band in ND$_3$ would be expected in the region 2350-2400 cm^{-1} which underlies the Hg line adjacent to ν_1.

A component of the antisymmetrical stretching vibration ν_3 was observed at 3375 cm^{-1} in NH$_3$ and 2507 cm^{-1} in ND$_3$. This vibration gives rise to a species E and two species F phases of coupling. Since the observed lines occur so near the corresponding infrared active vibrations at 3278 and 2500 cm^{-1}, they may arise from the same F component observed in the infrared spectrum. However, since in all cases the observed splitting between components was very small, it may be that the bands arise from either of the other components or from a superposition of the three. The frequency found for ν_3 in the crystal in this and the previous paper are in accord with that recently found in the gas from its Raman spectrum.[6]

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6. C. Cumming & H. L. Welsh, J. Chem. Phys., <u>21</u>, 1119 (1953)

The lines at 3303 and 3369 cm^{-1} reported by Sutherland[2] certainly correspond to those at 3160-3330 cm^{-1} and 3375 cm^{-1} in the work reported here. Sutherland assigned the line he observed at 1585 cm^{-1} to ν_4, which like ν_3' may have three active Raman components in the crystal. No line was observed in this region in the present work. Since Sutherland did not observe the lines at 1058 and 1048 cm^{-1} at all, any comparable Raman scattering in the present study in the vicinity of 1585 cm^{-1} would be expected to be more intense than the lines around 1050 cm^{-1}. Sutherland observed the spectrum at -185°C. whereas the present study was performed at -82°C.; therefore the possibility remains that the relative intensities of the lines around 1050 cm^{-1} and 1585 cm^{-1} change enough with temperature to account for the apparent discrepancy,

although this seems highly improbable.

In addition to the well-defined features, the microphotometer trace shows a broad band with a maximum at about 2700 cm^{-1} (2730Å) which can be ascribed to $\nu_2 + \nu_4$. There may also be other diffuse bands running from 2630Å to 2670Å and from 2670Å to 2700Å. (1300-1900 cm^{-1}, 1900-2300 cm^{-1}).

Lattice Vibrations

As pointed out before, there are five fundamental lattice vibrations originating in molecular torsion, three of symmetry species F and one each of species A and E, and four fundamental lattice vibrations originating in molecular translation, two of species F and one each of species A and E. (There are actually three species F translational vibrations but one of them is the zero frequency motion corresponding to translation of the crystal as a whole.) Because of its small moments of inertia, one expects the translational motions in these molecules to be of lower frequency than the torsional motions, although the two types of motion of a given symmetry species may be coupled. These motions may also be coupled to the internal vibrations of the molecules of the same symmetry species, but because of the large frequency separation it is doubtful if such coupling is of any consequence.

As seen in Table 1, a number of lattice vibrations were observed. A complete assignment of the observed bands is not possible but several features should be noted. From the low frequency and the small frequency separation between NH$_3$ and ND$_3$ the bands at 99 and 129 cm^{-1} in NH$_3$ and 91 and 121 cm^{-1} in ND$_3$ are certainly translational modes. The Teller-Redlich ratios of the species A and E translations are both 1.084 and the ratio for the two species

F translations is 1.177. The observed ratios of the above two bands are both 1.08. Although the symmetry of the bands cannot be determined, the observed ratios indicate that there is very little coupling between the translational and torsional lattice modes.

From the high intensity, relatively high frequency and large frequency shift in going from NH_3 to ND_3, the bands at 284 cm^{-1} in NH_3 and 213 cm^{-1} in ND_3 are almost certainly fundamental torsional modes. The observed frequency ratio of these bands is 1.33. The Teller-Redlich product ratio for the species A torsion is 1.41. for the species E torsion is 1.39 and for the three species F torsions is 2.736. Although again it is not possible to determine the symmetry of the motion, the observed ratio indicates that it is a nearly uncoupled torsion.

The band between 325 and 375 cm^{-1} in NH_3 almost certainly arises in part from the species F torsion observed at 362 cm^{-1} in the infrared spectrum[1]. The high frequency shoulder of the corresponding band in ND_3 was observed in the infrared spectrum but the position of the band center could not be determined because the low frequency limit of the spectrometer used was 300 cm^{-1}. The band between 245 and 270 cm^{-1} in the Raman spectrum of ND_3 corresponds to the band between 325 and 375 cm^{-1} in NH_3. This indicates that the band center of the species F torsion in ND_3 is approximately 260 cm^{-1}.

There was no evidence of Raman scattering corresponding to the bands observed at 527 and 406 cm^{-1} in the infrared spectrum of NH_3 and ND_3 respectively. These bands must be of species F but it is doubtful if they are fundamental vibrations. The remaining low frequency bands in the Raman spectrum of NH_3 and ND_3 are probably

combinations and overtones of lattice fundamentals.

In conclusion, the interaction between the molecules in the NH_3 and ND_3 crystals must be small. Not only is the separation between the different phases of coupling of the internal vibrations small but also it appears that the low frequency translational and torsional modes are only slightly coupled.

TABLE 1

Observed Raman Bands of Crystalline Ammonia and 3-Deutero-Ammonia

NH_3

Assignment*	Observed Frequency, Raman (cm^{-1})		Observed Frequency, Infrared (cm^{-1})
lattice vibrations	99	s	53+ / 52
	129	m	--+
	284	vs	250+ / 250+
	325–375	w	362+ / 362+
	~386	vw	--
	430–462	vw	527
	--		
ν_2'	1048	s	--
ν_2	1058	m	1060
ν_4	--		1646
ν_1', ν_3, ν_4	3160–3330	s	--
ν_1	--		3223
ν_3, ν_3' or ν_3''	3375	s	3378 (ν_3)

ND_3

Assignment*	Observed Frequency, Raman (cm^{-1})		Observed Frequency, Infrared (cm^{-1})
lattice vibrations	91.5	s	41+
	121	m	--
	142–161	vw	--
	213	vs	--+
	245–270	w	200
	280–312	w	<300
	330–380	w	--
	--		406
	505–540	vw	--
ν_2'	810	s	--
ν_2	817	m	815
ν_4	--		1196
ν_1'	2330	s	--
ν_1	--		2318
ν_3, ν_3 or ν_3''	2507	vs	2500 (ν_3)

* $\nu_1, \nu_2, \nu_3, \nu_4$ refer to the internal modes of NH_3, species F if unprimed, species A if single primed and species F if double primed.

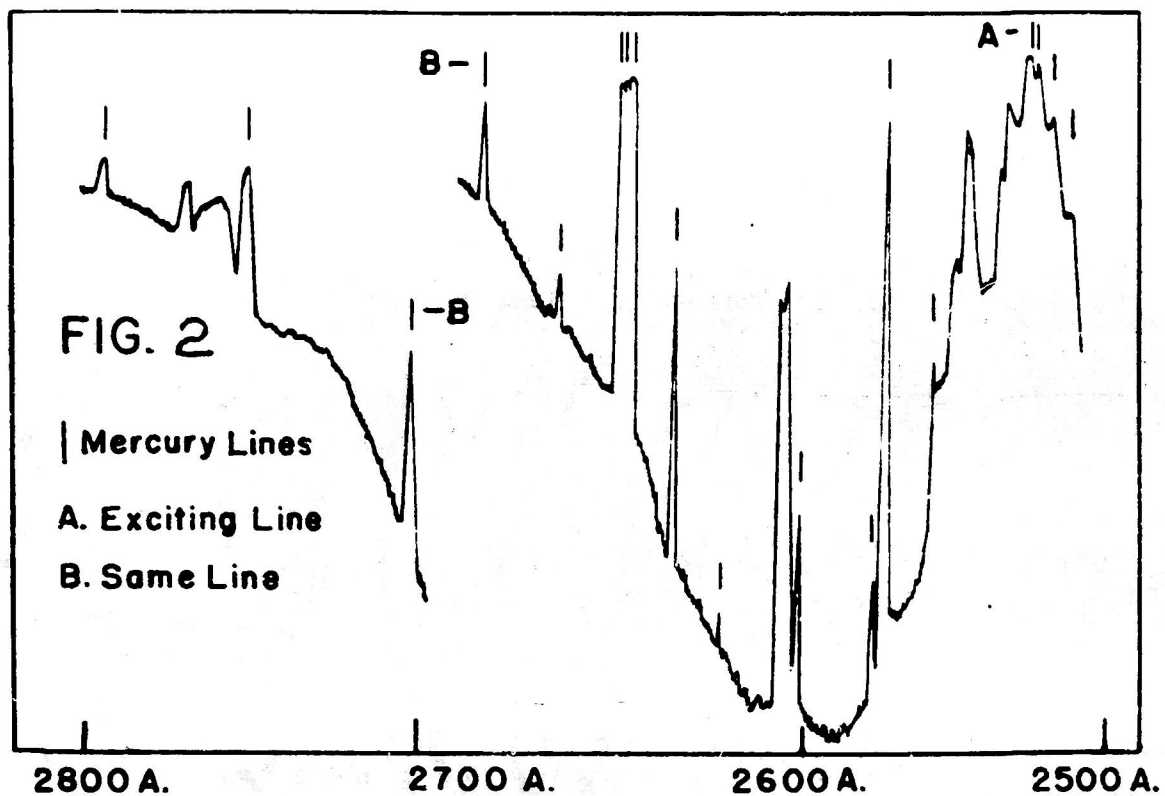+ From Combination bands in the infrared spectrum.

Figure 1
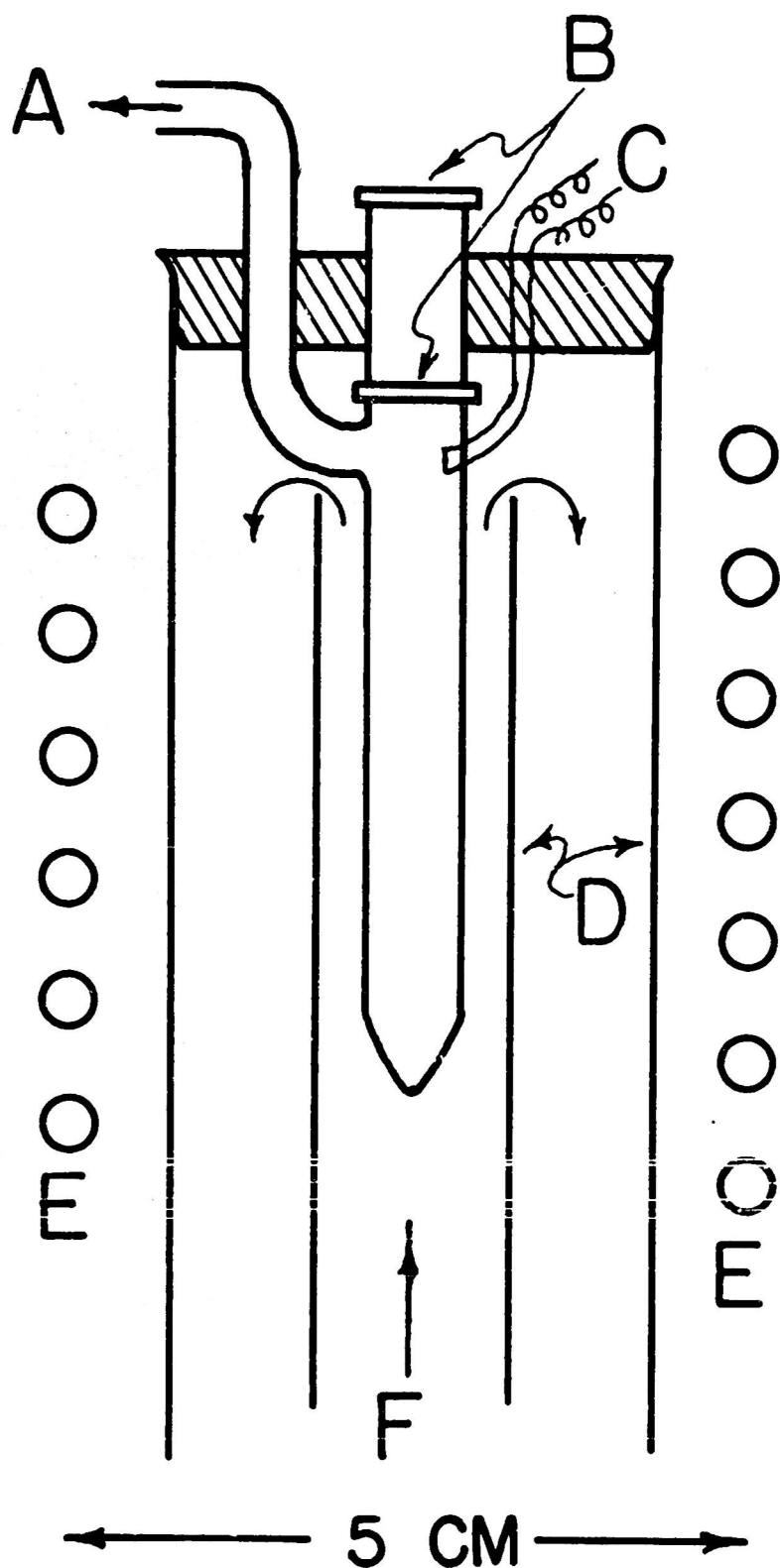
A. To NH$_3$ Reservoir.
B. Double quartz window with dead air space to avoid frosting.
C. Thermocouple.
D. Quartz baffle.
E. Helical quartz lamp.
F. Cold nitrogen.

RAMAN SPECTRUM OF NH₃

FIG. 2

| Mercury Lines

A. Exciting Line

B. Same Line

2800 A.   2700 A.   2600 A.   2500 A.

RAMAN SPECTRUM OF ND₃

FIG. 3

| Mercury Lines

A. Exciting Line

B. Same Lines

2700 A.   2600 A.   2500 A.